DEVELOPMENT OF $TiNb_2O_7$ ANODE FOR LITHIUM ION BATTERY ANODES

UNDERGRADUATE HONOR THESIS

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Abstract

With an increase in gasoline price and greenhouse gas emissions, hybrid electrical vehicles (HEV) and pure electric vehicles (EV) have been commercialized in auto market. Li-ion batteries have become the dominant power source for the EV applications because of many advantages such as high energy densities, less pollution, stable performance and long cycle life. However, the market for HEVs and EVs need to overcome many technical issues. For example, energy densities and cycle life of Li-ion batteries need to be improved at low temperature for electrical vehicle applications. $TiNb_2O_7$ (TNO) electrode-based battery can be a good choice in order to improve the energy densities and cycle life. The original anode-based batteries are $Li_4Ti_5O_{12}$ (LTO) anode-based batteries. I have made a comparison between TNO anode and LTO anode for Li-ion batteries. The energy densities of TNO anode-based batteries are around 350Wh/L and the energy densities of LTO anode-based batteries are around 177Wh/L. It means that TNO anode-based batteries have a higher energy density than LTO anode-based batteries. In addition, TNO anode batteries have a longer cycle life and shorter charging time than LTO anode batteries. The purpose of this research is to identify whether the TNO anodes-based batteries have the advantage of high energy and power densities for Li-ion batteries application. First, I need to identify whether the TNO anode can be run in normal cycling battery by doing half-cell test. I have done the half-cell test which consist of TNO anode and metallic Li as a counter electrode. The voltage profile obtained from half-cell test fits well with TNO electrode. In addition, cycle life tendency corresponding to high-density TNO composite electrode which indicate the TNO electrode can be used in normal cycling battery. In the future research study, I will identify the important parameters that lead to poor performance in the low-temperature condition and demonstrate the performance of TiNb2O7 anodes-based batteries has been improved in the low temperature condition.

Dedication

The document is dedicated to my friends, family, and significant other.

Acknowledgments

I would like to thank my advisor, Dr. Jung Hyun Kim, who gave me the opportunity to work in his lab for 1 year and supported me throughout the entire process. When I am confused about the research process, he is very patient to explain for me. I can get a big progress on the research work because his insight, advice and encouragement.

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Introduction

With increasing in gasoline price and greenhouse gas emission, more and more electrical vehicles appear on the Auto market Rechargeable Li-ion batteries are the leading candidate for electrical vehicles due to their high energy density, long cycle life and less pollution compared with other battery chemistries. However, a large market of HEVs and EVs requires to overcome many kinds of problems existed in Li-ion batteries such as external force, low temperature, overcharging and overdischarging. Among these issues, the low temperature condition cause significant loss of battery power, accelerate the decay rate and cause chemical reaction to proceed more slowly. Therefore, the battery will produce less current which will cause the mechanical energy to decrease. The electrochemical properties of $TiNb_2O_7$(TNO) have been studied in order to develop an alternative anode with good performance at low temperatures. The $TiNb_2O_7$ composite electrode consists of micro-size spherical TNO secondary particles which exhibit high-rate capability, long cycle-life and a high volumetric capacity. TNO exhibits a high theoretical capacity of 387.6 mAh/g based on 5 Li insertion per formula unit for electron transfer of Ti^{4+} /Ti^{3+}, Nb^{5+}/ Nb^{3+} redox couples [1]. Practically, over 280 mAh/g is possible with a working potential of around 1.55V vs. Li, irrespective of the synthetic procedures employed [2-11]. However, TNO has poor ionic and electronic conductivity in practice. Automotive applications for HEVs and EVs need high volumetric energy density. In order to improve the electronic conductivity, TNO secondary particles will be coated with carbon. TNO secondary particles with carbon coating are expected to produce high-density electrode because the micro-size sphere particles have a high tap density and allow a reduction of the amount of carbon conductor and binder additives. This research project will address some issues such as poor conductivity of TNO and will make an evaluation of the electrochemical properties of TNO

electrodes. The effect of TNO batteries at various temperatures and the performance of TNO batteries at low temperatures will be figured out.

The goal of this research study was to identify whether the TNO anode-based battery can have a good performance in low temperature condition. To pursue this research goal, there are four objectives during this research. First, I need to do a synthesis of phase pure $TiNb_2O_7$ with controlled particle size. Second, I would apply carbon coating on the TNO powder to improve electronic conductivity. Then I would characterize the electrochemical performance of TNO as anodes in Li-ion battery cells. Finally, the performance of TNO needs to be evaluated at various temperatures which is ranged from -30℃ to 55℃.

Experimental Methodology

To identify the TNO anode-based battery can do a good performance in low temperature condition, I need to prove that TNO anode can be used in normal cycling battery. After that, I will apply carbon coating on TNO powder to improve the electronic conductivity. Finally, the carbon coated TNO anode-base battery will be run at low temperature such as -30℃. The performance of TNO anode-based battery can be evaluated by some images such as voltage profile, cycle life and coulombic efficiency.

Synthesis of phase pure $TiNb_2O_7$ powder

To do a synthesis of TNO powder, there is a reaction between TiO_2 anatase and niobium pentoxide (Nb_2O_5). Then it was mixed in Ethyl Alcohol and mashed by using spex mill. The mixture was heated at 1100℃ in KSL-1700X muffle furnace shown in Figure 1 for 12 h to obtain TNO powder. The color of TNO powder is white. Before making TNO electrode, I need to identify whether the phase of TNO powder is homogeneous phase. The TNO powder can be

identified in homogeneous phase by using X-ray diffraction (XRD) test. The XRD test can characterized the crystalline phase of TNO. It also can make an analysis between TNO with carbon coating and TNO without carbon coating. I have obtained the XRD images of TNO powder that I made and theoretical XRD images of pure phase of TNO powder. The Figure 2 (a) shows that the XRD image of TNO powder that I have made. The Figure 2 (b) shows that the theoretical images of pure phase of TNO powder. The peak intensities are matched with each other in XRD images, which can clearly prove the TNO powder is in homogeneous phase. In order to figure out the shape of TNO powder, I have done the scanning electron microscopy (SEM) test and obtained SEM micrographs at different magnification of pure TNO powder shown in Figure 3.

Figure 1: KSL-1700X muffle furnace

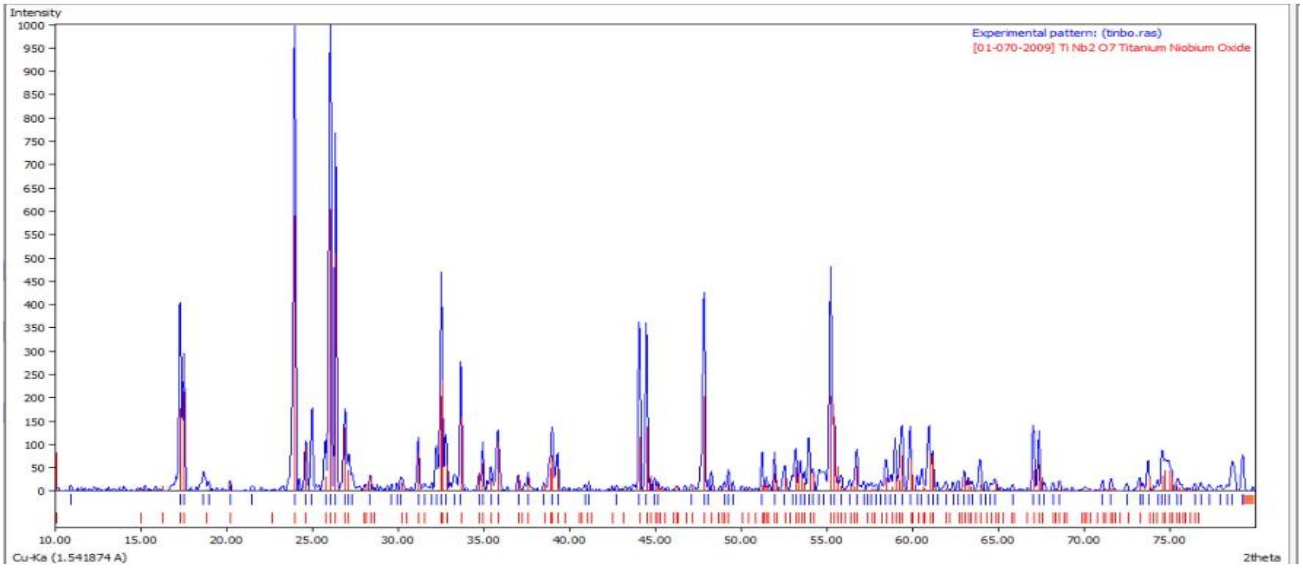


Figure 2(a): XRD pattern of TNO power that was made

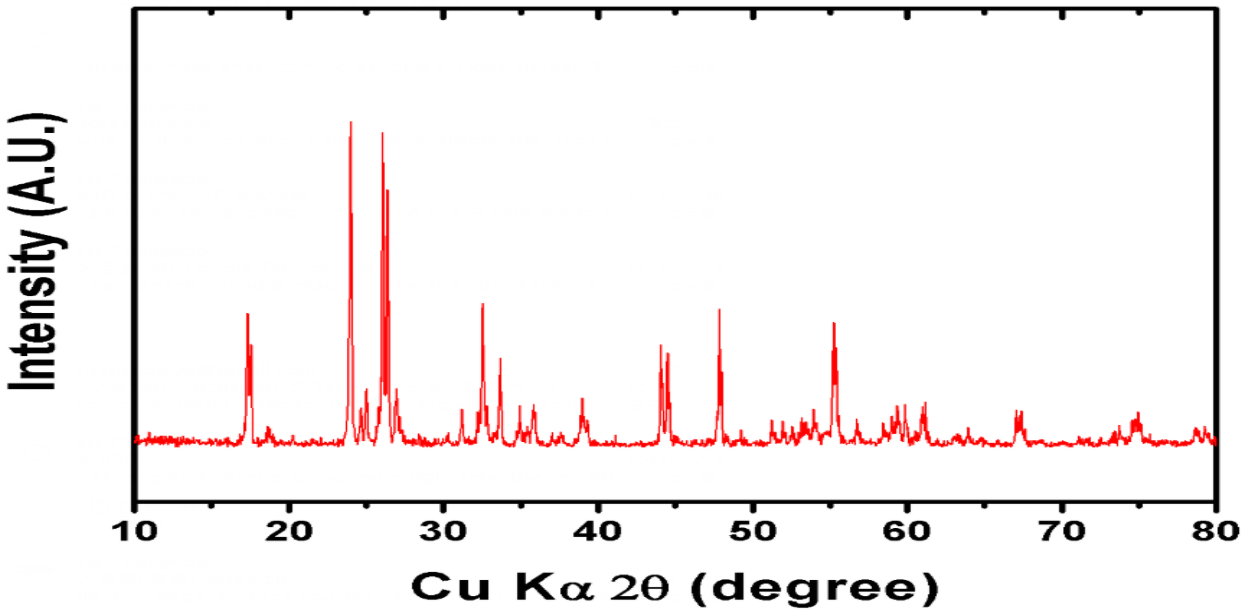


Figure 2(b): XRD pattern of phase pure TNO powder

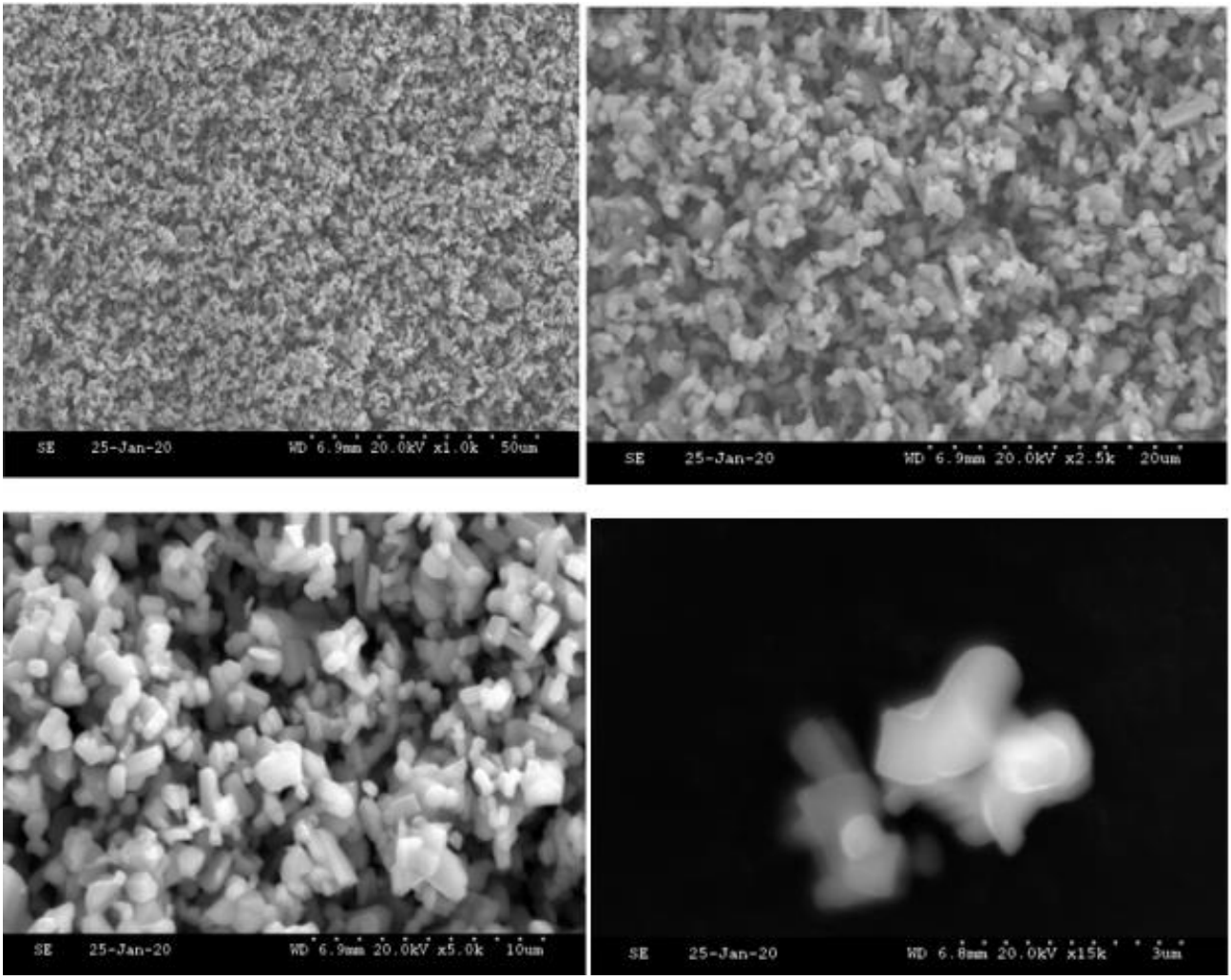


Figure 3: SEM images at different magnification of Pure TNO powder

TNO Electrode Making

The TNO electrode can be made by using TNO powder, conductor graphite (carbon black) and PVDF binder. The conductor graphite is used to improve the electrical conductivity. The PVDF provide a good adhesion between electrode film and separator. First, I need to weigh all material by using different concentration ratio. High density TNO composite electrode (HD-TNO) have larger mass concentration of TNO power than low density TNO composite electrode (LD-TNO). I have tried different weight ratios such as TNO powder: conductor graphite: PVDF

binder=85%: 7.5%: 7.5. During the first TNO electrode making process, I weighed the TNO powder-0.51g, conductor graphite-0.045g, and PVDF binder-0.045g. Then I added 0.5mL NMP to the mixing powder, which improve the solubility of the solution. The next step is to use the planetary vacuum mixer to do roll milling. Then I used Dr. Blade to attach anode material to copper foil. Finally, I dried the anode material at 80℃ for around 1 hour in vacuum oven shown in Figure 4.

Figure 4: Vacuum Oven for drying the anode material

Coin Cell making

The coin cell making process involved many steps. First, I placed the top of the battery case in an upside-down direction. Then I put a ring and one spacer on the top case. Next, I placed the TNO anode material on the spacer (black side upward) and added $LiPF_6$-ethylene carbonate (EC)-ethyl methyl carbonate (EMC) electrolytes to TNO anode. Then I will put a separator on the top of TNO anode which is used to separate the Li cathode and TNO anode. The Li metal will be placed on the top of separator. Finally, I attached the bottom case and clamp the battery by using crimper. Figure 5 shows the whole process of coin cell making.

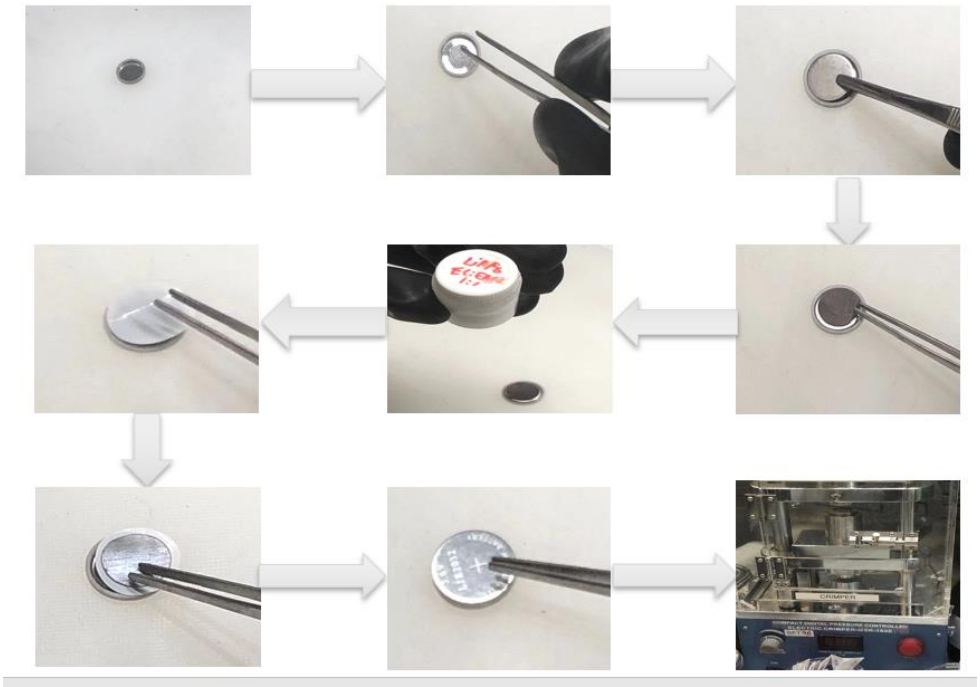


Figure 5: Coin Cell Making Process

Coin Half-Cell Test

Before introducing the concept of coin half-cell test, I want to explain the difference between half-cell test and full cell test. The half-cell test consists of TNO anode and metallic Li as a

counter electrode. The full-cell test consists of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM) cathode and TNO anode. Both these two tests can evaluate cycle life, power capability and the performance of charging and discharging in the electrical vehicle applications. The coin half-cell test includes different process. The initial rest is to stabilize the TNO battery which can make electrolyte fully contact with anode and cathode. The discharge process is to extract the Lithium-ions. The charging process is to insert the Lithium-ions into TNO anode. The charge-discharge rate tests of TNO composite electrode was carried out between 1 and 3V at 0.2 C rate.

Carbon Coating

The sample of TNO particle with carbon coating can be prepared by coating sucrose and burning it out at high temperature in inert gas atmosphere using a tubular furnace. First, The TNO powder and $C_{12}H_{22}O_{11}$ (sucrose) were dissolve in distilled water. Then, the solution was mixing homogeneously by using magnetic bar and heated at 80℃ for 24h. The purpose of heating process is to evaporate the water and to obtain the pure substances only including $TiNb_2O_7$ and carbon. Then I used the tubular furnace shown in Figure 6 to do carbon coating. The inert gas is Argon gas which is input into tubular furnace to empty the air inside the furnace. This process is to prevent the reaction between oxygen with carbon. The carbon is very important for the carbon coating process and need to be remained. Before carbon coating, we need to seal the input and output of tubular furnace and check whether the Argon inert gas is enough. Otherwise, the carbon will have a reaction with oxygen. During the carbon coating process, I set the initial temperature and time consuming of tubular furnace. The initial temperature is 25℃ and maximum temperature is 700℃. The temperature started to increase from 25℃ to 700℃, which took 3 hour and 45 minutes. Then the TNO powder was heated at 700℃ for 2 hours. Finally, the temperature decreased from 700℃ to 25℃, which took another 3 hours and 45 minutes. The

color of the sample particle has changed to black after the carbon coating process, which is shown in Figure (6). There is a black thin carbon layer outside the active material particle, which can be observed by using transmission electron microscopy (TEM). N. Takami et al. [1] has already characterized TNO particles by using TEM, as illustrated in Figure 7. Figure 7 (c) and (d) show TEM images of TNO particles with no carbon coating and carbon coating.

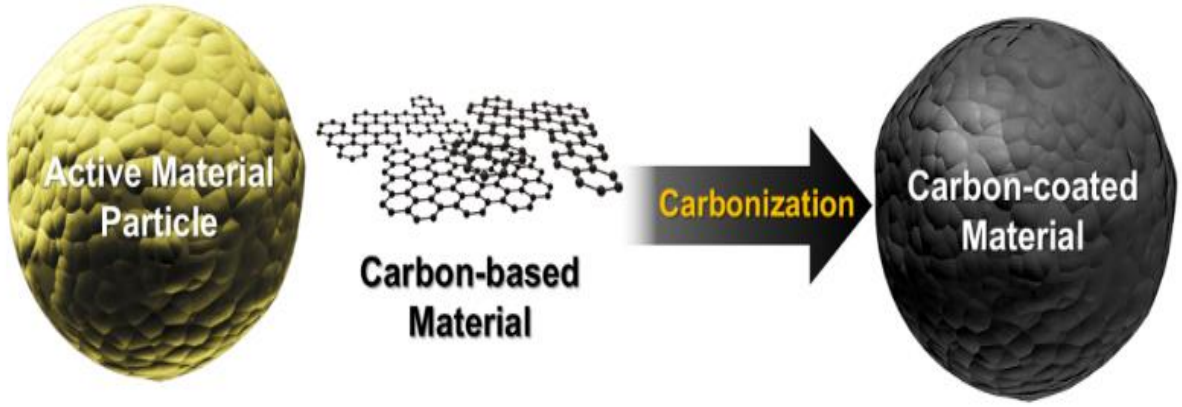


Figure 6: Conceptual image for carbon coating process.

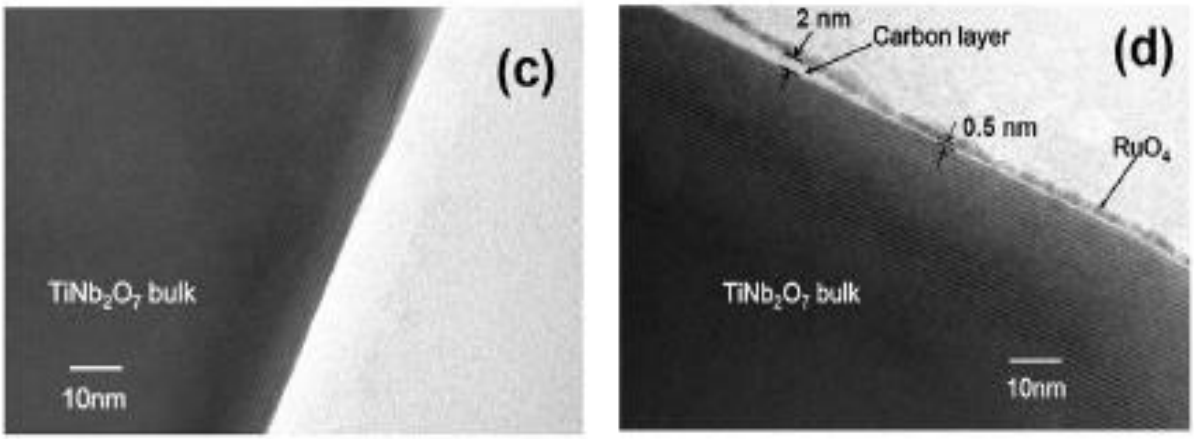


Figure 7: (c) TEM image of TNO particles with no carbon coating. (d) TEM image of TNO particles with carbon coating [1].

Results and Discussion

I have done coin half-cell tests of TNO anode without carbon coating and TNO anode with carbon coating. The electrochemical performance including the voltage profile, cycle life, dQ/dV analysis and coulombic efficiency can be evaluated from coin half-cell tests. In addition, the electrochemical performance of TNO anode can be optimized by using different TNO anodes that were made by using different concentration ratio (TNO powder: conductor graphite: PVDF binder).

Performance of TNO anode half-cell without carbon coating

The first TNO composite electrode was prepared from a mixed slurry of 85 wt% TNO powder, 7.5 wt% conductor graphite, 7.5 wt% PVDF binder in an aqueous solution. Using this TNO electrode-based battery, several performance images can be obtained from coin half-cell test.

Figure 8(a) shows that specific discharge capacity of TNO anode-based cell gradually decreases when the cycle number increases. Each cycle includes one charging process and one discharging process. Compared with the theoretical testing condition in article shown in Figure 8(b), the testing process shows that our cell has the similar capacity fading tendency (50% after 10 cycles). The similar fading tendency shows that our TNO particles synthesized successfully. However, the quick fading shows that the electrical conductivity among TNO particles are not ideal. The carbon coating may overcome this problem. In addition, the beginning low specific capacity of our cell is because of the low proportion of graphite conductor in our cell, which is 7.5 wt% compared with 20 wt% conductor graphite in article. The lower conductivity conducts less charges, so the specific capacity will be less. In Figure 8(b), the high-density TNO electrode in article was prepared with just 5 wt% conductor which shows large improvement in specific

capacity compared with low density TNO electrode which is prepared with 20 wt% conductor. Figure 8(b) also shows specific capacity retention of the TNO composite electrode with carbon coating and no carbon coating during charge-discharge cycling at 0.2 C rate. The rate capabilities and cycle performance of TNO composite electrodes with carbon coating were significantly superior to those of TNO composite electrodes with no carbon coating. Figure 9(a) shows that our voltage profile has a similar plateau which indicates the two-phase coexistence region compared with the profile of lithium extraction in article shown in Figure 9(b). It also shows two one-phase reaction corresponds to the article's, which can indicate our TNO particle synthesized successfully. From Figure 9(a), the voltage increases quickly during charging process and decreases quickly during discharging process because of the large impedance of the TNO anode-based battery. In addition, the voltage of the beginning of discharge is around 2V which is lower than the theoretical voltage which is 3V. The voltage drop at the beginning of discharge indicates the self-discharging from reaction inside the cell. This self-discharging reaction's product may also influence the battery performance. In Figure 9(c), there are several peaks which are corresponding to different phase reaction in voltage profile.

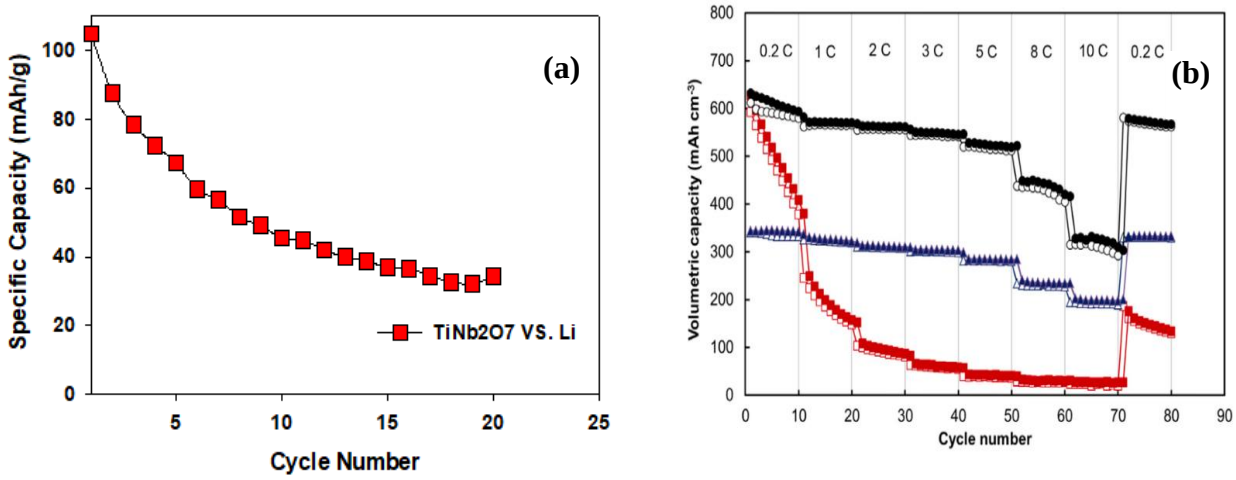
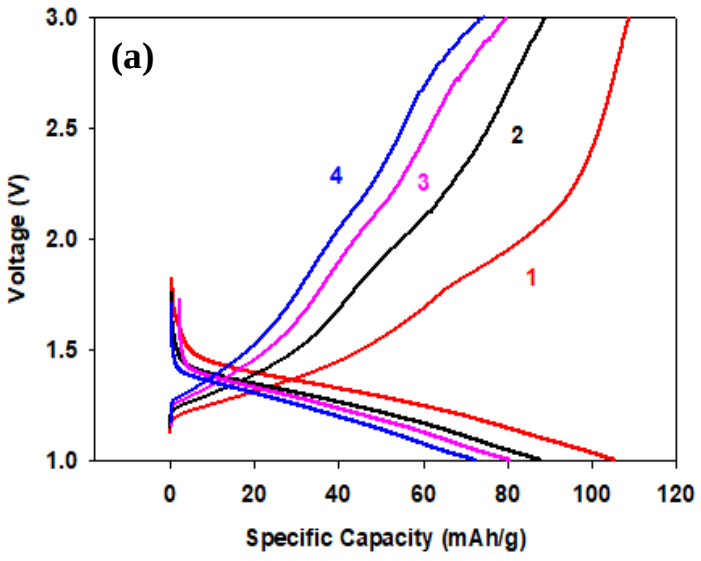


Figure 8: (a) Capacity retention of TNO anode without carbon coating. (b) Theoretical Capacity retention of TNO anode without carbon coating in article [1].

The second TNO composite electrode was prepared from a mixed slurry of 70 wt% TNO power, 10 wt% conductor graphite, 20 wt% PVDF binder. The difference between the first TNO electrode and the second TNO electrode is weight percent of TNO powder and conductor graphite. Compared with the first TNO electrode, the weight percent of the second TNO composite electrode decreased from 85 wt% to 70 wt%. Figure 10(a) shows the specific capacity of TNO anode prepared by low proportion of TNO powder. Compared the specific capacity of HD-TNO with specific capacity of LD-TNO, it can conclude that the specific capacity of TNO battery can be improved by increasing the mass concentration of TNO powder, which overcomes the shortcoming of less capacity from non-active materials (binder, conductor). Figure 10(b) shows that the voltage of LD-TNO increases so fast that the two-phase coexistence reaction and two one-phase reaction cannot be happened. The quicker voltage increasing/decreasing indicates the larger impedance which means that the performance of LD-TNO is not ideal.



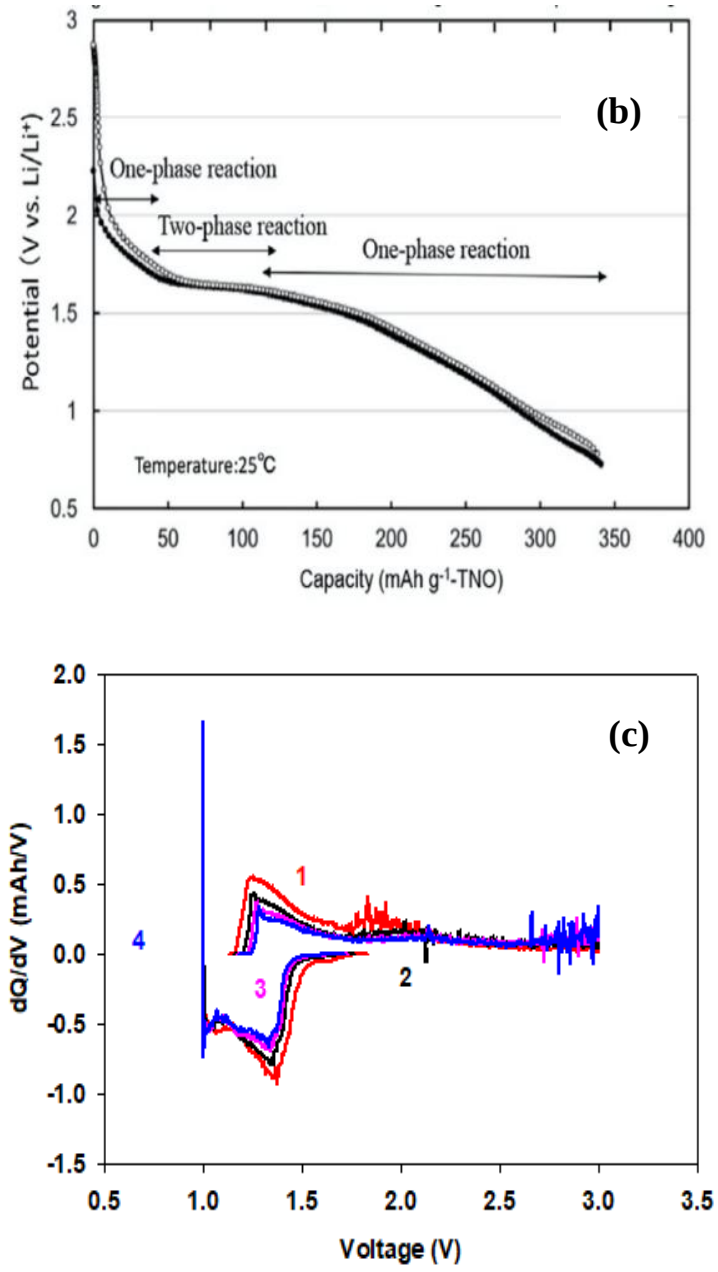
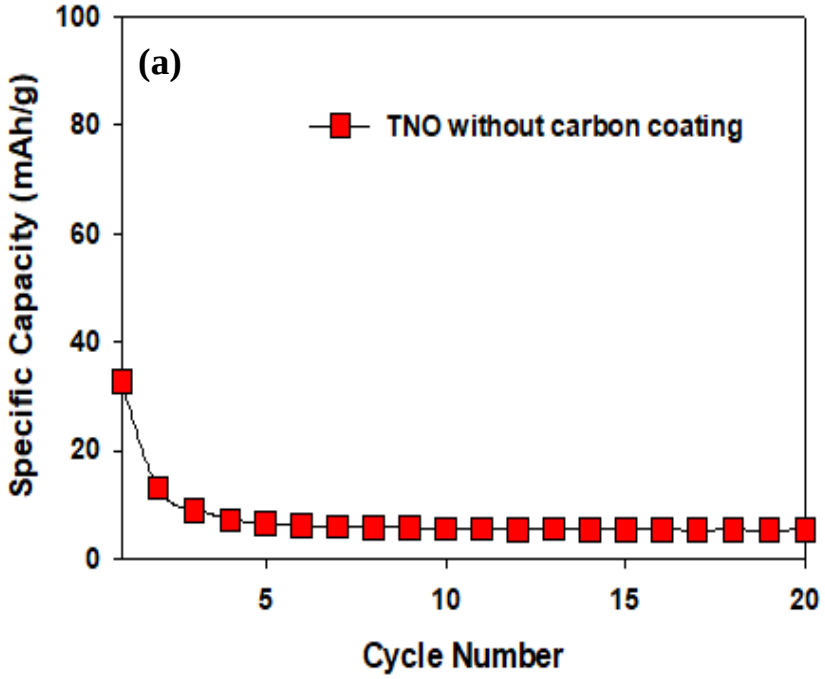


Figure 9: (a) Open-circuit plots of TNO electrode during lithium insertion and extraction. (b): Open-circuit plots of HD-TNO electrode during lithium insertion and extraction at 15mA/g [1]. (c) dQ/dV analysis of TNO electrode-base battery.



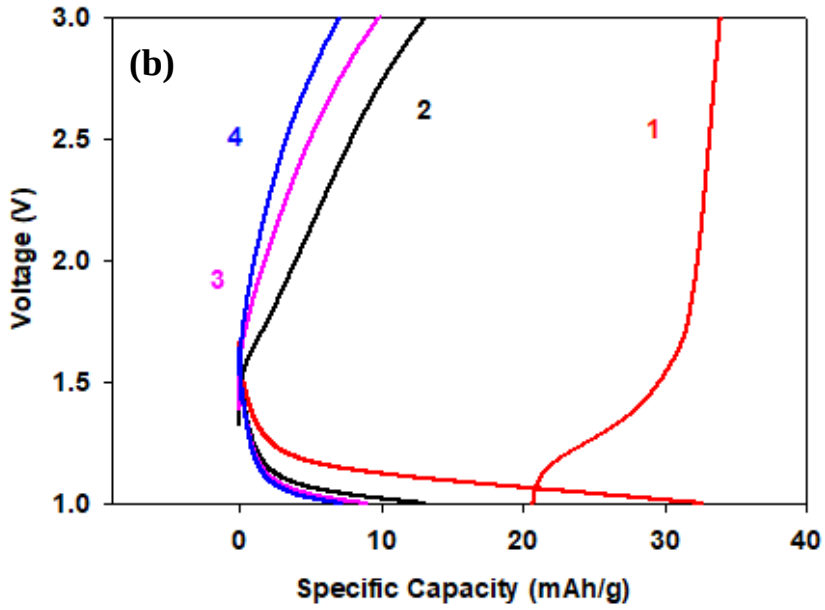


Figure 10: (a) Capacity retention of LD-TNO anode without carbon coating. (b) Open-circuit plots of LD-TNO electrode during lithium insertion and extraction.

Performance of TNO anode half-cell with carbon coating

The performance of TNO anode with carbon coating is not ideal because of several problems during the carbon coating process. First, the input and output of tubular furnace are not sealed very well. Then the Argon inert gas is not enough for the whole carbon coating process. Both cases caused a reaction between oxygen and carbon. Therefore, the color of the TNO powder after carbon coating is not black. Although the carbon coating process is not totally successful, the performance of TNO composite electrode has improve a lot compared to the performance of TNO composite electrode without carbon coating. The TNO carbon coating plot in Figure 11 shows that the specific capacities of the TNO composite electrodes with carbon coating were significantly superior to those of TNO composite electrodes with no carbon coating, which is attributed to improved electrical conduction among TNO particles due to the carbon coating. Another two plots called TNO 1st try and TNO 2nd try in Figure 11 prove that the specific discharge capacities of the first TNO composite electrode is larger than those of the second TNO composite electrode because of the higher mass concentration of TNO powder as mentioned before.

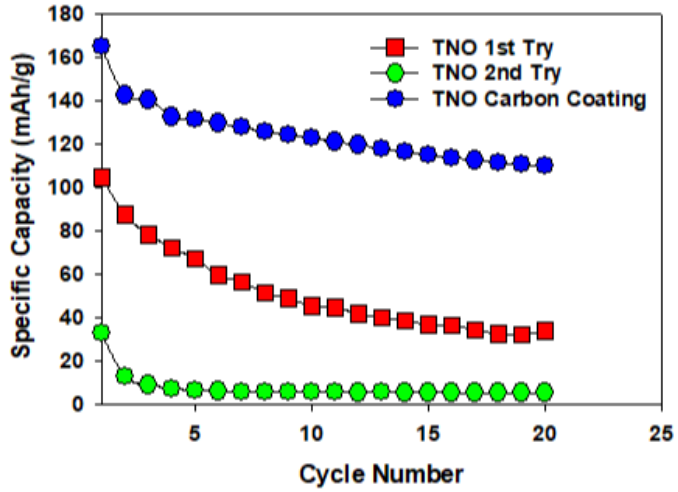


Figure 11. Capacity retention of TNO 1st try and TNO 2nd try and TNO carbon coating by charge-discharge cycling at 0.2 C rate between 1 and 3 V.

Performance of TNO anode half-cell with carbon coating

During this carbon coating process, I have solved those two problems mentioned before. My graduate partner has bought the Argon inert gas which is enough for the whole carbon coating process. In addition, I used the high vacuum grease to seal the input and output of the tubular furnace, which can provide good lubricating and sealing ability. However, I do not have enough time to finish the carbon coating process. As I mentioned before, N. Takami et al. [1] have explored the improvement of specific capacities after carbon coating of TNO electrodes and concluded that the specific capacities of TNO composite electrode with carbon coating were significantly superior to those of TNO composite electrode with no carbon coating, which is shown is Figure 8(b). Therefore, we can predict that the specific discharge capacities will be much larger than those of the undesirable carbon coating if the carbon coating process is ideal.

Conclusion

The electrochemical properties of $TiNb_2O_7$(TNO) have been studied in order to develop an alternative anode with good performance at low temperatures. The electrochemical performance of half-cell test proved that the TNO anode can be run in normal cycling battery. In order to improve the specific discharge capacities, the TNO need to be carbon coated and the mass concentration of TNO powder need to be increased.

Future experimentation is necessary to completely prove the TNO anode-base battery can be applied to electrical vehicles at low temperatures. First, different mass concentration of TNO powder need to be investigated for better specific capacities. Then the carbon coating process need to be improved through sealing and temperature setting. Finally, the full-cell test which consists of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$(NCM) cathode and TNO anode needs to be done in low temperature. The electrochemical performance including the voltage profile, cycle life, dQ/dV analysis and coulombic efficiency need to be obtained and evaluated, which can prove that TNO anode-based battery can have good performance at low temperatures in the future study.

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